

# Post density functional theoretical studies of highly polar semiconductive $\text{Pb}(\text{Ti}_{1-x}\text{Ni}_x)\text{O}_{3-x}$ solid solutions: The effects of cation arrangement on band gap

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## Abstract

We use a combination of conventional density functional theory (DFT) and post-DFT methods, including the local density approximation plus Hubbard  $U$  (LDA+ $U$ ), PBE0, and self-consistent  $GW$  to study the electronic properties of Ni-substituted  $\text{PbTiO}_3$  (Ni-PTO) solid solutions. We find that LDA calculations yield unreasonable band structures, especially for Ni-PTO solid solutions that contain an uninterrupted  $\text{NiO}_2$  layer. Accurate treatment of localized states in transition-metal oxides like Ni-PTO requires post-DFT methods.  $B$ -site Ni/Ti cation ordering is also investigated. The  $B$ -site cation arrangement alters the bonding between Ni and O, and therefore strongly affects the band gap ( $E_g$ ) of Ni-PTO. We predict that Ni-PTO solid solutions should have a direct band gap in the visible light energy range, with polarization similar to the parent  $\text{PbTiO}_3$ . This combination of properties make Ni-PTO solid solutions promising candidate materials for solar energy conversion devices.

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## Introduction

The bulk photovoltaic effect (BPVE) has been observed in ferroelectric perovskite oxides such as  $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$  [1–3],  $\text{LiNbO}_3$  [4] and  $\text{BaTiO}_3$  [5]. This effect has attracted increasing research interest, in view of its potential application for solar energy conversion devices. As incident light is absorbed by a single-phase ferroelectric material, the photo-excited electrons and holes are spontaneously separated, preventing recombination, and producing a photovoltaic effect. One ferroelectric material extensively studied for this purpose is  $\text{BiFeO}_3$ . It has a strong polarization  $\approx 0.9 \text{ C/m}^2$  [6, 7] and a direct band gap  $\approx 2.67 \text{ eV}$  [8]. Recent experiments have demonstrated the BPVE of  $\text{BiFeO}_3$  under visible incident light [9–11]. However,  $\text{BiFeO}_3$  is one of very few ferroelectric materials that have both large spontaneous polarization and small  $E_g$ . Most solid oxide ferroelectrics are wide-gap insulators ( $E_g > 3.0 \text{ eV}$ ) that absorb very little of the visible spectrum.

Recent theoretical work on  $\text{Pb}(M_x\text{Ti}_{1-x})\text{O}_{3-x}$  perovskite solid solutions ( $M=\text{Ni}$ ,  $\text{Pd}$  and  $\text{Pt}$ ) provides a promising strategy for designing highly polar semiconducting oxides [12, 13]. By substituting the *B*-site  $\text{Ti}$  with an O-vacancy-stabilized  $d^8 M^{2+}$  cation, the resulting system displays a decreased  $E_g$  when compared to  $\text{PbTiO}_3$  (PTO), while retaining a large polarization. Of these proposed materials, Ni-PTO solid solutions possess great potential for practical solar applications, as they can be synthesized from relatively inexpensive raw materials. However, due to the strongly correlated Ni-3*d* electrons, Ni-PTO has a complex electronic structure that is not captured by standard LDA calculations [14]. In this study, we explore the electronic structure of Ni-PTO solid solutions with post-DFT calculations, including LDA+*U*, PBE0 hybrid functional and self-consistent *GW*. We predict the band gap and other electronic properties for Ni-PTO solid solutions of various compositions and *B*-site orderings, to guide future experimental synthesis and measurement.

## Methodology

We perform first-principles calculations with a plane-wave basis set, as implemented in the Quantum-Espresso [15] and ABINIT [16] codes. The LDA exchange-correlation functional is used for structural relaxations, with a  $6 \times 6 \times 6$  Monkhorst-Pack k-point grid [17] and a 50 Ry plane-wave cutoff. All atoms are represented by norm-conserving [18] opti-

mized nonlocal [19] pseudopotentials, generated with the OPIUM code [20]. The electronic contribution to the polarization is calculated following the Berry’s phase formalism. [21, 22]

Several supercell configurations are used, including  $1\times 1\times 2$  and  $1\times 1\times 3$  layered structures (with  $B$ -cation alternation along (001) direction); rocksalt ( $\text{Pb}_2\text{NiTiO}_5$ ),  $\sqrt{2}\times\sqrt{2}\times 2$  and  $2\times 2\times 2$  structures ( $\text{Ni-O}_5$  cages are separated by  $\text{Ti-O}_5$  cages). By studying these configurations, the effects of different compositions and  $B$ -site cation orderings can be investigated. Post-DFT methods are then applied to these Ni-PTO systems. In the next section, we briefly describe each post-DFT method, to facilitate comparison of results obtained with each method.

## Results and Discussion

### Post-DFT methods

Before applying post-DFT methods to Ni-PTO, we study its parent materials, tetragonal  $\text{PbTiO}_3$  and cubic  $\text{NiO}$ , as reference systems to evaluate the performance of post-DFT methods for related materials. We do so because it is known that the Kohn-Sham (KS) band gap determined by the conventional LDA method is systematically underestimated by 50-100 % [23, 24]. To improve the quality of the electronic structure description of Ni-PTO, especially the treatment of correlation for the localized Ni-3*d* orbitals, we employ LDA+ $U$ , the PBE0 hybrid functional, and self-consistent  $GW$  (sc- $GW$ ) methods.

#### LDA+ $U$

The LDA+ $U$  method is a computationally inexpensive way to improve the DFT-LDA band gap. A simplified version of the rotationally invariant formulation of the LDA+ $U$  method [14] is employed in the present work, where  $U$  is assigned to be the value of the spurious curvature of the total energy of the system with respect to the variation in the number of electrons ( $n_i$ ) in a localized orbital. [25] The effective interaction parameter  $U$  is determined by the change of orbital occupations  $n_i$  with respect to an external potential  $\alpha_j$  projected onto the corresponding localized level:

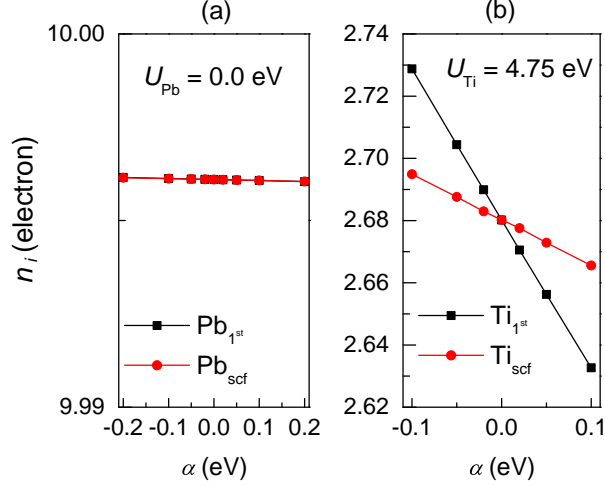


FIG. 1: (Color online) The occupation number ( $n_i$ ) of localized  $d$ -orbitals for Pb and Ti in  $\text{PbTiO}_3$ , with respect to potential shift  $\alpha$ . Shown as (black) squares are the values obtained using self-consistent (scf) relaxation, and shown as (red) circles are those without ( $1^{\text{st}}$ ), for constructing  $\chi$  and  $\chi_0$  respectively.

$$U = (\chi_0^{-1} - \chi^{-1})_{ii}, \quad \chi_{ij} = \frac{dn_i}{d\alpha_j}, \quad (1)$$

Here the  $\chi_{ij}$  are the elements of the linear response matrix,  $n_i$  is the occupation number of the localized levels at site  $i$  and  $\alpha_j$  represents the potential shift applied on the localized orbital at site  $j$ .  $\chi$  (the screened response matrix) includes all screening effects from the crystal environment which is associated with the localized electrons, and  $\chi_0$  (the unscreened response matrix) contains non-screening effects of the total energy of the non-interacting Kohn-Sham states associated with the system. The latter term can be computed from the first iteration in the self-consistent cycle.

Tetragonal  $\text{PbTiO}_3$  is selected as an example for detailed study. A  $2 \times 2 \times 2$   $\text{PbTiO}_3$  supercell is used, because it is large enough to give a converged linear response calculation of  $U$ . Fig. 1 displays the calculated  $U$  values for Pb and Ti atoms of  $\text{PbTiO}_3$ . In the rotationally invariant LDA+ $U$  method, on-site interaction energy  $E_U \propto U \cdot [\lambda(1-\lambda)]$ . For fully occupied orbitals such as Pb  $5d$ ,  $\lambda = 1$ , so on-site correction plays no effect. As displayed in Fig. 1 (a), the number of electrons on the Pb  $5d$  orbitals will not change with respect to the external potential  $\alpha$ , so  $U=0$  eV. Ti has partially filled  $3d$  orbitals, so it has a non-zero  $U$

TABLE I: Hubbard  $U$  terms (in eV) for Ni and Ti in  $\text{PbTiO}_3$ ,  $\text{NiO}$  and Ni-PTO solid solutions, obtained with the linear-response approach.

Composition	$U_{\text{Ti}}$	$U_{\text{Ni}}$
$\text{PbTiO}_3$	4.75	-
$\text{NiO}$	-	5.70
layered $\text{Pb}_2\text{NiTiO}_5$	4.85	9.31
rocksalt $\text{Pb}_2\text{NiTiO}_5$	4.85	8.92
$1 \times 1 \times 3$ $\text{Pb}_3\text{NiTi}_2\text{O}_8$	4.75	9.35
$\sqrt{2} \times \sqrt{2} \times 2$ $\text{Pb}_4\text{NiTi}_3\text{O}_{11}$	4.75	8.86
$2 \times 2 \times 2$ $\text{Pb}_8\text{NiTi}_7\text{O}_{23}$	4.77	8.91

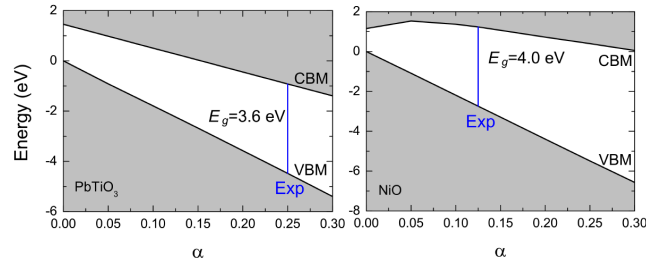


FIG. 2: (Color online) Valence band maximum (VBM) and conduction band minimum (CBM) versus PBE0 functional exact-exchange fraction  $\alpha$  for  $\text{PbTiO}_3$  and  $\text{NiO}$ . Vertical lines represent the experimental band gaps, illustrating how  $\alpha_0$  is chosen (see Table II).

value.

Following the procedure above, using the self-consistent linear response method, as implemented in Quantum-Espresso, the Hubbard  $U$  terms for Ti and Ni in  $\text{NiO}$ , PTO, and all Ni-PTO solid solutions can be determined (see in Table I).

#### *PBE0 hybrid density functional with exact-exchange*

DFT-LDA does not include exact exchange. This is unlike the PBE0 functional, which includes a linear combination of exact-exchange and GGA-PBE exchange [26]. The electron

TABLE II: Band gaps (in eV) of PbTiO<sub>3</sub> and NiO, calculated using LDA, PBE0 (with the optimal fraction of exact exchange  $\alpha_0$ ) and sc-*GW* methods.

	LDA	PBE0 ( $\alpha_0$ )	sc- <i>GW</i>	Exp.
PbTiO <sub>3</sub>	1.46	3.50 (0.25)	3.82	3.60 [30]
NiO	1.16	3.98 (0.125)	4.14	4.0-4.3 [31, 32]

correlation term is the same as that of PBE functional [27]:

$$E_{xc}^{\text{PBE0}} = \alpha E_x + (1 - \alpha) E_x^{\text{PBE}} + E_c^{\text{PBE}}. \quad (2)$$

where  $\alpha$  is the fraction of exact exchange. As PBE0 includes a portion exact exchange, it can greatly reduce the self-interaction error of LSDA or GGA functional, and therefore greatly improves the calculated band gap for most semiconductors and insulators. [27] However, due to the long-range nature of the exact-exchange interaction and resultant large computational cost, (about one to two orders of magnitude more than LDA in the present work) PBE0 calculations are mainly applied to periodic systems with small unit cells, such as those described in the present study. [28]

In the original PBE0 functional,  $\alpha=0.25$ . However, it is argued that there is no universal  $\alpha$  that is applicable for all materials [29]. In order to predict band gap values for new materials more accurately, it is considered useful to select an  $\alpha$  that yields accurate band gaps for the relevant prototype systems. Fig. 2 shows the  $\alpha$  dependence of the conduction and valence band edges of PbTiO<sub>3</sub> and NiO. Comparing with experimental band gap values, we obtain an optimal  $\alpha_0=0.25$  for PbTiO<sub>3</sub> and 0.125 for NiO (Fig. 2 and Table II).

### *Self-consistent GW*

It is widely believed that the self-consistent *GW* method is the most accurate way to obtain electronic band structures, since it includes both the non-locality and dynamical correlations absent in DFT-LDA. Therefore, obtaining the self energy,  $\Sigma$ , is the key quantity of any *GW* calculation. It was shown by Hedin *et al.* that the self-energy can be represented as a product of the Green's function  $G$  and the screened Coulomb interaction  $W$ ,  $\Sigma = iGW$ . [33]

Since our system has a complicated electronic band structure, in which the band gap is dictated by the bonding interactions between the correlated Ni  $3d$ -states and O  $2p$ -states, the self-consistent  $GW$  (sc- $GW$ ) method probably gives the most accurate quasi-particle (QP) electronic structures of Ni-PTO.

Following the methodology developed by Lebegue *et al.*, [34] we employ the contour deformation method [35, 36], as implemented in ABINIT, to perform the numerical integral for the self-energy. Within this scheme, the contour of the frequency integral for self-energy is deformed into integrals along the imaginary and real axes. The numerical integral along the imaginary axis can be evaluated by Gaussian quadrature. We find that integrating up to 114 eV and using 10 quadrature points yields converged results for the imaginary axis. The real axis integral is calculated by summing values of the Coulomb screening at a uniform mesh of frequencies, with a mesh spacing of 1.25 eV, from 0 to 120 eV.

This upper limit of real axis integration is chosen from spectral function data, [35, 36] (electron energy loss data in the present work), since the correlation part of the self-energy can be represented by a spectral function.

Due to the expensive computational cost (three to four orders of magnitude more than DFT-LDA in the present work), we restrict sc- $GW$  calculations to only one Ni-PTO system – rocksalt structure. For this configuration, 400 bands are included, with a plane-wave cutoff of 25 Ha for the QP and LDA states, and a  $2 \times 2 \times 2$  Monkhorst-Pack k-point grid. [17] As LDA calculations can qualitatively predict a correct semiconducting ground state for rocksalt Ni-PTO (Fig. 6), we choose to represent the initial QP wave functions in the basis set of LDA wave functions. QP band gaps are converged to within 0.05 eV.

### Comparison of results for parent end members

Fig. 3 shows the projected density of states (PDOS) for tetragonal  $\text{PbTiO}_3$  and cubic  $\text{NiO}$ , calculated with the LDA, PBE0 and LDA+ $U$  methods, from which we can evaluate the accuracy of each post-DFT method. Experimental studies show that tetragonal  $\text{PbTiO}_3$  is an insulator with an indirect band gap ( $X \rightarrow \Gamma$ ) of 3.60 eV. [30] LDA severely underestimates this band gap value by more than 50%. The LDA+ $U$  method gives a better band gap value than LDA, but is still lower than PBE0, which comes closest to experiment. This is because the exact-exchange in PBE0 is applied to all states, whereas the Hubbard  $U$  of LDA+ $U$

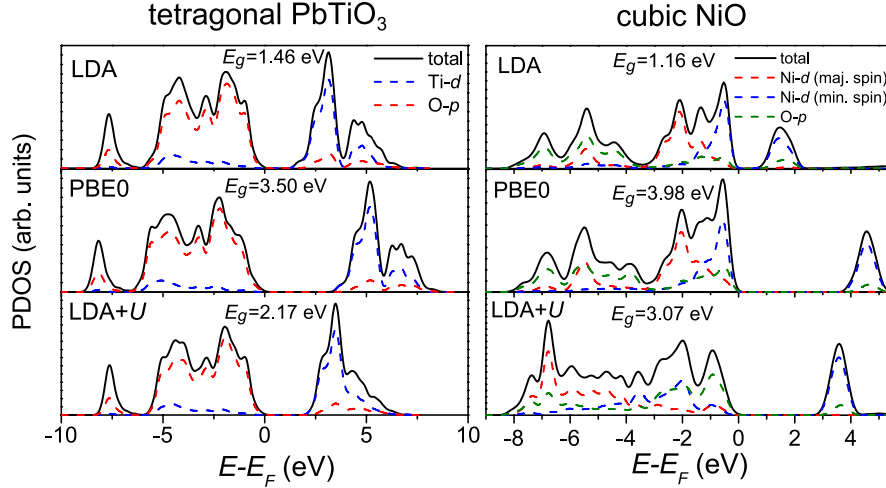


FIG. 3: (Color online) Band gap values and orbital-resolved PDOS of tetragonal  $\text{PbTiO}_3$  and cubic  $\text{NiO}$  using LDA, PBE0 and LDA+ $U$ . For PBE0 calculations, the optimal  $\alpha_0$  values are used.

acts directly *only* on the localized Ti-3d orbitals. Also, when compared to PBE0, LDA+ $U$  significantly alters the PDOS for  $\text{PbTiO}_3$ , especially for Ti-3d and O-2p states.

$\text{NiO}$  is an anti-ferromagnetic insulator with an experimentally measured band gap between 4.0 and 4.3 eV [31, 32]. As shown in Fig. 3, LDA predicts a band gap of 1.16 eV and LDA+ $U$  predicts 3.07 eV, while PBE0 (with  $\alpha_0=0.125$ ) reproduces the experimental band gap. For both LDA and PBE0 functionals, the PDOS has a clear split between majority spin Ni  $t_{2g}$  and  $e_g$  orbitals, while the band gap of the system falls between occupied minority-spin  $t_{2g}$  and empty  $e_g$  orbitals. Applying the Hubbard  $U$  to the Ni-3d orbitals increases the  $\text{NiO}$  band gap, relative to LDA. However, LDA+ $U$  predicts Ni-d spectral weight located at a relatively low energy (2 – 8 eV below  $E_F$ ). This is in contrast to both experimental photoemission spectra [37] and theoretical dynamical mean field theory (DMFT) results [38]. These studies suggest that there should be a strong Ni-d contribution to the valence band of the system. Though LDA+ $U$  does predict a larger band gap than DFT-LDA, it does not reproduce the salient aspects of the experimental valence-state spectrum of  $\text{NiO}$ .

### Electronic properties of $\text{Pb}_2\text{NiTiO}_5$ solid solutions

We begin our study of Ni-PTO with the smallest supercell configuration:  $\text{Pb}_2\text{NiTiO}_5$ . In this solid solution, half of the  $\text{Ti}^{4+}$  cations are replaced by O-vacancy-stabilized  $\text{Ni}^{2+}$



cations [12]. This polar substitution will generate a  $V_{\text{O}}^{\bullet}$  and  $\text{Ni}_{\text{Ti}}^{\prime\prime}$  defect pair (in Kroger-Vink notation [39]), where the lowest-energy configuration corresponds to the local dipole parallel to the overall polarization ( $\vec{P}$ ). The Ni-PTO structure is tetragonal, with a large polarization similar to the parent  $\text{PbTiO}_3$  (Table IV). After replacing  $\text{Ti}^{4+}$  with  $\text{Ni}^{2+}$ , the remaining apical O will move away from  $\text{Ni}^{2+}$ , making Ni coordination nearly square planar. Since this O atom shifts opposite to the cations, it further increases  $\vec{P}$ . For  $\text{Pb}_2\text{NiTiO}_5$ , two different *B*-site cation orderings are studied: (i)  $1 \times 1 \times 2$  layered and (ii) rocksalt Ni-PTO.

Layered Ni-PTO is structurally similar to the planar nickelate  $\text{SrNiO}_2$ . A previous theoretical study of  $\text{SrNiO}_2$  predicted it to be a diamagnetic insulator with fully occupied  $d_{xz}$ ,  $d_{yz}$ ,  $d_{xy}$  and  $d_{z^2}$  orbitals, leaving  $d_{x^2-y^2}$  empty. [40] Accordingly, since layered Ni-PTO is a nickelate with planes of  $\text{Ni}^{2+}$  ions, we anticipate that it should have an insulating ground state.

Fig. 4 (a) shows the band structure for layered Ni-PTO along high-symmetry directions in the Brillouin zone (BZ). The LDA band structure reveals a two-dimensional character: the energy bands are highly dispersive in the  $k_x$ - $k_y$  plane, but show a very weak  $z$ -axis dispersion along  $\Gamma$ - $Z$ . One strongly dispersive band (dashed line in Fig. 4 (a)) crosses  $E_F$ , making the system metallic in LDA. This band is chiefly composed of  $\text{Ni-}3d_{x^2-y^2}$  and  $\text{O-}2p$ . Isosurfaces for this band at  $\Gamma$ , X and M points are displayed in Fig. 4 (b). There is a pronounced hybridization between  $\text{Ni-}d_{x^2-y^2}$  and  $\text{O-}p$ , as the lobes from  $\text{Ni-}d_{x^2-y^2}$  are directed towards the four O ions. Specifically, the wave functions at X and M consist of  $\text{O}(p_x)\text{-Ni}(d_{x^2-y^2})\text{-O}(s+p_z)$  and  $\text{O}(p_x)\text{-Ni}(d_{x^2-y^2})\text{-O}(p_y)$  orbital combinations respectively, both of which display anti-bonding character. However, there is a strong bonding profile between  $\text{Ni-}d_{x^2-y^2}$  and  $\text{O-}p_z$  at the  $\Gamma$  point ( $\text{Ni}$  red (blue) to  $\text{O}$  red (blue) lobes), which indicates that electron density is shared between  $\text{O-}2p$  and  $\text{Ni-}d_{x^2-y^2}$  orbitals, again according to LDA calculations.

LDA calculations show that for layered Ni-PTO, the band gap is zero. We find that in LDA calculations, the energy level of the  $\text{Ni-}d_{x^2-y^2}$  orbital is quite low, permitting this low-lying orbital to backbond with  $\text{O-}p_z$  orbitals. This enhancement of the bonding interaction between  $\text{Ni-}3d_{x^2-y^2}$  and  $\text{O-}2p$  causes LDA to predict a metallic ground state for layered Ni-PTO.

In our LDA+ $U$  calculations, applying the Hubbard  $U$  term (determined to the  $\text{Ni-}3d$  orbitals, in a self-consistent linear response calculation [25]), yields a split between occupied and unoccupied  $\text{Ni-}3d$  states. This provides a better description of  $E_g$  for Ni-PTO, relative to

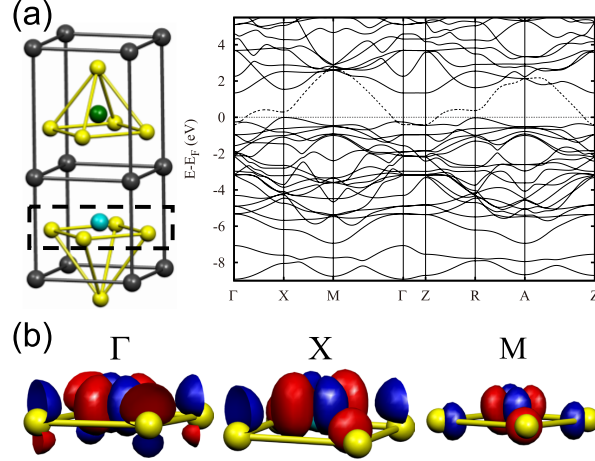


FIG. 4: (Color online) (a) Atomic structure of layered  $\text{Pb}_2\text{NiTiO}_5$ , and its DFT-LDA calculated electronic band structure. The band that crosses the Fermi level is shown as a dashed line. (b) The wave function isosurfaces are plotted for this band at  $\Gamma$ , X and M. For clarity, only the isosurface near the Ni-O<sub>2</sub> plane of the band indicated by the dashed lines in (a) is plotted. The isosurface values are  $\pm 0.04 \text{ e}/\text{\AA}^3$  (red and blue surfaces). The plots illustrate which atomic orbitals compose each eigenstate:  $\Gamma$ : O( $p_z$ )-Ni( $d_{x^2-y^2}$ )-O( $p_z$ ), X: O( $p_x$ )-Ni( $d_{x^2-y^2}$ )-O( $s+p_z$ ) and M: O( $p_x$ )-Ni( $d_{x^2-y^2}$ )-O( $p_y$ ). This series of images shows the drastic change in bonding from  $\Gamma$  to X to M. Pb, Ti, Ni and O atoms are represented as gray, green, cyan and yellow spheres respectively.

LDA. However, the PBE0 hybrid density functional, which includes exact-exchange energy, can significantly improve the description of  $E_g$  of ferroelectric oxides [41]. To obtain the most realistic results from a PBE0 calculation, the optimal exact-exchange mixing fraction  $\alpha$  from relevant prototype systems should be used. Unlike  $\text{PbTiO}_3$ , with  $E_g$  between occupied O-2*p* and empty Ti-3*d* states, both Ni-PTO and NiO have  $E_g$  between occupied and unoccupied Ni-*d* states. Therefore, we use NiO as our prototype parent system of Ni-PTO, and select  $\alpha=0.125$  for PBE0 calculations of Ni-PTO. A comparison of the eigenvalues at  $\Gamma$  obtained for the Ni 3*d*-states using LDA, LDA+*U* and PBE0 is presented in the supplementary material (EPAPS number).

Though the most computationally demanding of our post-DFT methods, the many-body *GW* approach is considered the most reliable first principles method to obtain electronic band structure, and it has been successfully applied to many kinds of oxides. [35]. In our present work, we also employ this method for the ground state calculation of rocksalt Ni-

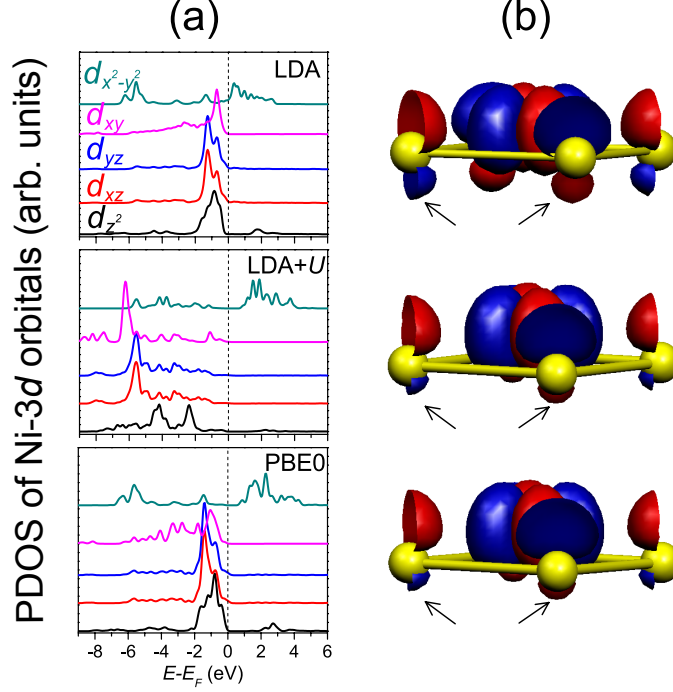


FIG. 5: (Color online) PDOS for Ni-3d and corresponding wave function isosurface for Ni- $d_{x^2-y^2}$  orbital (at  $\Gamma$ ) in layered  $\text{Pb}_2\text{NiTiO}_5$ , calculated using LDA, LDA+ $U$  and PBE0 hybrid density functionals respectively. Compared to LDA, LDA+ $U$  and PBE0 predict smaller downward red (blue)-lobes around planar O atoms (see arrows), indicating there is more O  $s$ - $p$  hybridization and a weaker bonding interaction between Ni- $d_{x^2-y^2}$  and O-2p.

PTO, obtaining a band gap of 1.83 eV. PBE0 predicts a value of 1.71 eV, improving upon the results obtained by LDA (0.69 eV) and LDA+ $U$  (1.59 eV), much closer to the sc-GW result.

Fig. 5 (a) shows the PDOS of Ni-3d in layered Ni-PTO, from LDA, LDA+ $U$  and PBE0 calculations. In both the LDA+ $U$  and PBE0 PDOS, the Ni- $d_{x^2-y^2}$  band lies above  $E_F$ , leading to the weaker bonding between Ni- $d_{x^2-y^2}$  and O-2p (Fig. 5(b)). Unlike LDA, which yields a metallic ground state for layered Ni-PTO, LDA+ $U$  and PBE0 predict an intrinsic semiconductor. Since the LDA+ $U$  and PBE0 results agree and are more consistent with the Ni- $d$  orbital paradigm in diamagnetic insulating  $\text{SrNiO}_2$ , [40] we consider LDA+ $U$  and PBE0 to be more accurate than LDA, and predict that layered Ni-PTO is a semiconductor.

The calculated PDOS shown in Fig. 5 also shows other prominent features. As a result of the hybridization between Ni and its planar coordinated O, the occupied Ni- $d$  orbitals,

such as  $d_{xz}$ ,  $d_{yz}$  and  $d_{z^2}$ , have a large band width of 2 eV (both LDA and PBE0 results). As the Ni ion is shifted up, away from the oxygen plane, the hybridization between Ni- $d_{z^2}$  and O- $p_z$  can give rise to bonding and antibonding states. The double peaks in  $d_{xz}$ ,  $d_{yz}$  states should correspond to bonding and antibonding states, which come from the hybridization between Ni- $d_{xz}$  ( $d_{yz}$ ) and O- $p_x$  ( $p_y$ ) (for details see the supplementary material). The strong hybridization between Ni and planar O ions indicate the covalency of Ni-O bonds in layered Ni-PTO.

After exploring the electronic properties of the layered structure, we extend our investigation to rocksalt ordered Ni-PTO (Fig. 6 (a)). In the layered structure, there is a strong *bonding* character between Ni- $d_{x^2-y^2}$  and O- $p_z$  (at  $\Gamma$ ). However, in rocksalt Ni-PTO, there is an *anti-bonding* relation between Ni- $d_{x^2-y^2}$  and O- $p_z$ , while bonding with O- $p_z$  occurs almost exclusively between Ti and O (Fig. 6 (b)). This hybridization pattern indicates that the electron density is mainly shared between Ti-3d and O-2p, and that the Ni- $d_{x^2-y^2}$  orbital is almost empty. This leads to the prediction of a semiconducting ground state for rocksalt ordered Ni-PTO, even at the LDA level (Fig. 6 (c)). A consistent picture emerges, as LDA+ $U$ , PBE0 and sc- $GW$  all predict rocksalt  $\text{Pb}_2\text{NiTiO}_5$  to be a semiconductor.

Besides the Ni- $d_{x^2-y^2}$  orbital, other Ni- $d$  bands also differ between the rocksalt and layered structures of Ni-PTO. In layered Ni-PTO, a strong hybridization between Ni and O yields energy bands with a large band-width. However, in rocksalt Ni-PTO, interrupting the  $\text{NiO}_2$  layer with Ti-O cages makes it more favorable for the filled O-2p orbitals to mix with the empty 3d orbitals of  $\text{Ti}^{4+}$  [42]. Therefore, Ni-3d orbital is weakly hybridized with O-2p, reducing its band width in rocksalt Ni-PTO (Fig. 6 (c)).

### ***B*-site cation ordering effects**

The results of our electronic band structure analysis indicate that different *B*-site cation orderings for  $\text{Pb}_2\text{NiTiO}_5$  systems can give rise to different degrees of Ni-O bond covalency. To support this, we calculate the Born effective charges (BECs) for *B*-site cations of Ni-PTO.

Since LDA incorrectly predicts a metallic ground state for layered Ni-PTO, the BECs and polarization  $\vec{P}$  of Ni-PTO should be calculated at the post-DFT level. The BEC tensor,  $Z_{\kappa,\alpha\beta}^*$ , is defined as the change in the macroscopic polarization along direction  $\alpha$  in response to a rigid displacement of a sublattice of atoms  $\kappa$  in direction  $\beta$ , times the unit cell volume

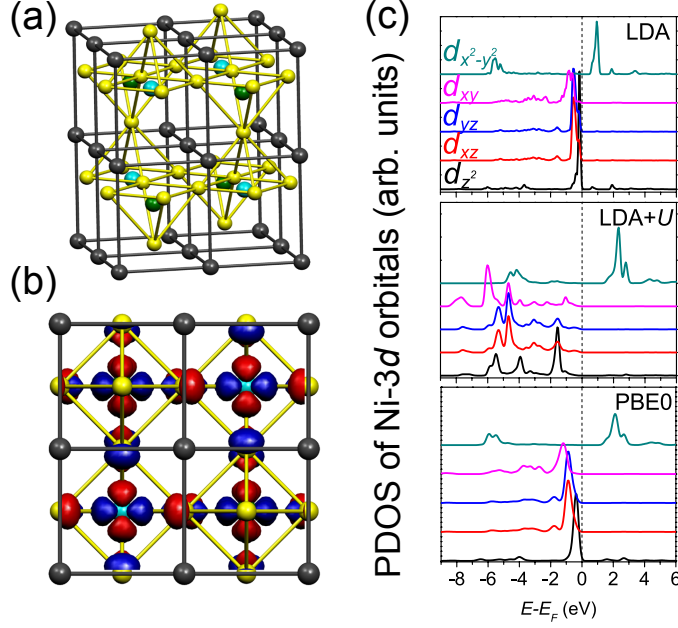


FIG. 6: (Color online) (a) Atomic structure of rocksalt  $B$ -site ordered  $\text{Pb}_2\text{NiTiO}_5$ . A  $2 \times 2 \times 2$  supercell containing 36 atoms is shown for clarity. (b) Isosurface of LUMO band (LDA results) at  $\Gamma$ . It is mainly composed of  $d_{x^2-y^2}$  orbitals, displaying anti-bonding character between  $\text{Ni-}3d_{x^2-y^2}$  and  $\text{O-}2p_z$ . (c) PDOS for  $\text{Ni-}3d$  orbital, obtained using LDA, LDA+ $U$  and PBE0 functional calculations respectively.

$\Omega_0$  [43]:

$$Z_{\kappa,\alpha\beta}^* = \Omega_0 \frac{\partial P_\alpha}{\partial \tau_{\kappa,\beta}} \Big|_{\vec{E}=0} \cong \Omega_0 \frac{\Delta P_\alpha}{\Delta \tau_{\kappa,\beta}} \Big|_{\vec{E}=0} \quad (3)$$

Following this definition,  $Z^*$  can be estimated by the finite-difference method: each atom  $\kappa$  is displaced slightly from its equilibrium position by  $\Delta \tau_\beta$ , and the resulting change in polarization  $\Delta P_\alpha$  can be calculated using the Berry-phase method. [21, 22] The displacement should be small enough to ensure the validity of the linear treatment of Eq. (3). For each structure, the  $U$  value is determined by a linear-response calculation, so that LDA+ $U$  calculations can generate an insulating ground state for all Ni-PTO structures. In this way, we calculate both  $Z^*$  and  $\vec{P}$  at the LDA+ $U$  level.

Table III gives the calculated non-zero BECs for Ni ions in Ni-PTO systems. As  $\text{Ni}^{2+}$  ion strongly favors a four-fold coordinate environment, its planar BEC tensor elements ( $Z_{xx}^*$  and

TABLE III: The Born effective charges  $Z^*$  of Ni cations in Ni-PTO solid solutions.  $Z^*$  is calculated using LDA+ $U$  finite difference methods.

Composition	$Z_{xx}^*$	$Z_{yy}^*$	$Z_{zz}^*$
$1\times 1\times 2$ $\text{Pb}_2\text{NiTiO}_5$	2.29	2.29	0.44
$1\times 1\times 3$ $\text{Pb}_3\text{NiTi}_2\text{O}_8$	2.33	2.33	0.37
rocksalt $\text{Pb}_2\text{NiTiO}_5$	2.14	2.14	0.86
$\sqrt{2}\times\sqrt{2}\times 2$ $\text{Pb}_4\text{NiTi}_3\text{O}_{11}$	2.17	2.17	0.72
$2\times 2\times 2$ $\text{Pb}_8\text{NiTi}_7\text{O}_{23}$	2.15	2.15	0.78

$Z_{yy}^*$ ) are larger than its nominal charge, indicative of covalency for the planar Ni-O bonds. Since the apical O moves away from Ni to create a square planar environment, the bonding between Ni and the apical O is weak. In the finite-difference simulation of  $Z^*$ , when Ni ion moves closer to the apical O, the electron density will transfer from Ni to O. Because of this negative charge density flow, the Ni ion will have a  $Z_{zz}^*$  smaller than its nominal charge. Moreover, the following trend is identified: as  $B$ -site cations change from layered to rocksalt ordering, there is a decrease of the planar BEC tensors of Ni, and an increase of  $Z^*$  along Ni-O vacancy direction. This trend is in good agreement with the bond covalency results we obtained above, that layered Ni-PTO has a more covalent Ni-O bond and larger  $Z_{xx}^*$  and  $Z_{yy}^*$  tensor for Ni, while less covalent Ni-O bond in rocksalt structure leads to the smaller in-plane Ni BECs.

In perovskite  $ABO_3$  compounds, a more ionic  $B$ -O bond usually yields a larger  $E_g$ , while a more covalent  $B$ -O bond is associated with a smaller  $E_g$ . This trend has been verified for many perovskite systems, such as  $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$  [44] and sulfide perovskite  $\text{BaZrS}_3$  [45]. In light of this trend, we now examine the Ni-PTO solid solution systems.

$E_g$  of several Ni-PTO solid solutions are summarized in Table IV. Relative to PTO,  $E_g$  of Ni-PTO solid solutions are considerably reduced. For the rocksalt structure, LDA+ $U$ , PBE0 and sc- $GW$  calculations increase  $E_g$  (relative to LDA) by different amounts, and the trend in calculated  $E_g$  is: LDA < LDA+ $U$  < PBE0 < sc- $GW$ . Unlike the parameter-free sc- $GW$ ,

TABLE IV: Reported here are the  $c/a$  ratio, polarization  $P$  (in C/m<sup>2</sup>), as well as indirect  $E_g$  (in eV) calculated using different methods for all the Ni-PTO solid solutions under investigation. Also shown are tetragonal PbTiO<sub>3</sub> results. For Ni-PTO solid solutions, direct band gaps at  $\Gamma$  are given in parentheses. Structural parameters are obtained by LDA calculations and,  $P$  is calculated using the LDA+ $U$  finite difference method. We use the optimal  $\alpha$  for PBE0 calculation.

Composition	$c/a$	$P$	$E_g^{\text{LDA}}$	$E_g^{\text{LDA}+U}$	$E_g^{\text{PBE0}}$	$E_g^{\text{sc-GW}}$
PbTiO <sub>3</sub>	1.05	0.81	1.46(3.05)	2.17(3.80)	3.50(4.31)	
1 $\times$ 1 $\times$ 2 Ni-PTO	1.14	0.85	0.00(0.00)	0.70(1.19)	0.87(1.02)	
1 $\times$ 1 $\times$ 3 Ni-PTO	1.14	0.84	0.00(0.00)	0.52(1.57)		
rocksalt Ni-PTO	1.21	0.96	0.69(1.12)	1.59(2.65)	1.71(2.64)	1.83(2.70)
$\sqrt{2}\times\sqrt{2}\times 2$ Ni-PTO	1.12	0.90	0.84(0.97)	1.53(2.24)		
2 $\times$ 2 $\times$ 2 Ni-PTO	1.08	0.83	0.70(0.94)	1.60(1.90)		

$E_g$  results obtained from LDA+ $U$  and PBE0 fairly strongly depend on the computational parameters (exact-exchange mixing fraction  $\alpha$  for PBE0 and Hubbard  $U$  term for LDA+ $U$ ). In the present work, LDA+ $U$  and PBE0  $E_g$  are in good agreement with sc- $GW$  results, verifying our parametrization for these calculations. It is worth noting that even though LDA+ $U$  yields  $E_g$  similar to PBE0 and sc- $GW$ , LDA+ $U$  gives a more localized and perhaps less realistic DOS distribution (Fig. 5 (a) and Fig. 2 in supporting information). Therefore, we only use it to obtain the relative  $E_g$  trend, but do not rely on LDA+ $U$  for the precise electronic structure. Our calculated  $E_g$  exhibits obvious  $B$ -site ordering effects: layered Ni-PTO always has a smaller  $E_g$  than rocksalt ordered Ni-PTO, and the variation in Ni doping percentage has little impact on  $E_g$  value.

By comparing the BEC tensor and  $E_g$  results of Ni-PTO solid solutions, we can establish the relationship between  $B$ -site cation ordering and band gap. The electronic properties of Ni-PTO primarily depends on the Ni-O bonding. In layered Ni-PTO, there is a complete Ni-O-Ni network, and strong hybridization between Ni- $d$  and O- $p$  increases Ni-O bond covalency, yielding a smaller  $E_g$ . However, if the Ni-O-Ni network is interrupted by Ti-O bonds, the hybridization between the filled O-2 $p$  orbitals and the empty 3 $d$  orbitals of Ti<sup>4+</sup> will be more favorable [42]. As a result, there is a more ionic bond between Ni- $d$  and O- $p$ , and the system has a larger  $E_g$ .

Guided by the  $E_g$  trend obtained above, we estimate that the lower  $E_g$  limit of Ni-PTO solid solutions should come from the layered structure, which could potentially be synthesized via layer-by-layer deposition techniques; the upper  $E_g$  limit corresponds to the more ionic rocksalt ordering structure, which can perhaps be obtained with a thermal annealing process. According to our prediction, layered Ni-PTO should have a direct optical band gap comparable to bulk Si, and  $E_g$  of rocksalt ordered Ni-PTO is close to that of  $\text{BiFeO}_3$  [8]. In this way, Ni-PTO solid solutions should have direct band gaps in the visible light energy range, displaying semiconducting electronic properties.

## Conclusion

In conclusion, we present theoretical studies on the electronic properties of  $\text{Pb}(\text{Ni}_x\text{Ti}_{1-x})\text{O}_{3-x}$  solid solutions. We identify the relation between  $B$ -site cation ordering and  $E_g$  of Ni-PTO systems. We expect that this relation can be used as a guiding principle to understand  $E_g$  behaviors for many perovskite solid solutions. Based on our theoretical calculations, we predict that the Ni-PTO solid solution can offer both a large polarization and a direct band gap in the visible light energy range. This combination of properties indicates that high photovoltaic efficiency can be realized in solar devices based on  $\text{Pb}(\text{Ni}_x\text{Ti}_{1-x})\text{O}_{3-x}$  oxides.

Furthermore, we demonstrate that the standard DFT-LDA provides qualitatively incorrect electronic structure for layered Ni-PTO, and potentially other systems being investigated as possible components in solar harvesting devices. A more accurate treatment of the Ni-3d states of Ni-PTO required post-DFT LDA calculations to obtain reasonable band gaps. Of the work presented here, the LDA+ $U$  method is the least computationally expensive of the post-DFT methods, though it sometimes yields unreasonable crystal field splits and unphysical PDOS features. Though the most computationally demanding, sc- $GW$  yields band gap results that are closest to experiment. The band gap results of PBE0 are close to that of sc- $GW$  and reproduce salient spectral features of the PDOS, while the computational cost is less than that of  $GW$ . For the purposes of calculating accurate band gaps, we suggest that the PBE0 method is a reasonable compromise of accuracy and cost.



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**Supplementary materials - Post density functional theoretical studies of highly polar semiconducting  $\text{Pb}(\text{Ti}_{1-x}\text{Ni}_x)\text{O}_{3-x}$  solid solutions: The effects of cation arrangement on band gap**

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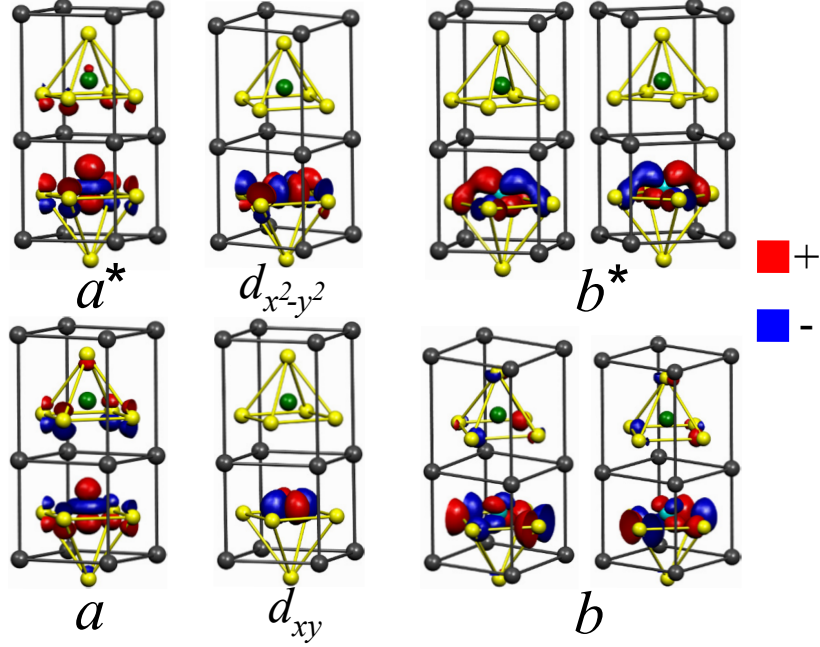


FIG. 1: (Color online) The wave function isosurfaces of the Ni-3d orbitals at  $\Gamma$  from the layered  $\text{Pb}_2\text{NiTiO}_5$ , calculated by LDA. The isosurface value is  $\pm 0.04 \text{ e}/\text{\AA}^3$ . Except for the non-bonding Ni-3d<sub>xy</sub> state, the wave functions show obvious hybridization between Ni-3d and O-2p.  $a$  and  $a^*$  correspond to the  $\pi$ -type bonding and antibonding states between Ni-3d<sub>z<sup>2</sup></sub> and O-2p<sub>z</sub>.  $b$  and  $b^*$  are degenerate bonding and antibonding states from Ni-d<sub>xz</sub> ( $d_{yz}$ ) and O-2p<sub>x</sub> ( $p_y).$

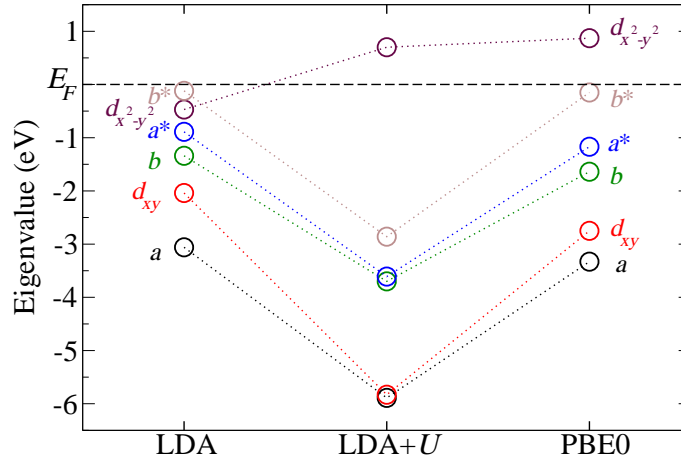


FIG. 2: (Color online) The energy levels (in eV) for the corresponding eigen states in Fig. 1, calculated by LDA, PBE0 and LDA+ $U$  methods. Fermi energy level is taken as energy zero. Both LDA+ $U$  and PBE0 predict an empty Ni- $d_{x^2-y^2}$  state. However, LDA+ $U$  predicts energy levels of occupied Ni- $d$  states far below the Fermi level, leading to the overall improper PDOS feature (Fig. 5 (a) in the main text) for layered Ni-PTO. Note that PBE0 has similar PDOS to LDA, and has  $d_{x^2-y^2}$  unfilled above  $E_F$ .